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Transport of $\text{Zn}(\text{OH})_4^{2-}$ ions across a polyolefin microporous membrane

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Abstract

Transport of $\text{Zn}(\text{OH})_4^{2-}$ ions through modified microporous polypropylene membranes was studied using polarography and conductometry. Soluble Nafion as an ion exchange modifying agent was applied to the membrane by several techniques. The influence of Nafion and surfactant on transport of zinc ions through the membrane was studied. A relationship between membrane impedance and the rate of $\text{Zn}(\text{OH})_4^{2-}$ transport was found. The found correlation between conductivity, ion permeability and Nafion coverage suggests a suitable technique of membrane preparation to obtain desired properties.

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Although primary cells with zinc electrodes are widespread, secondary systems based on the same materials still suffer from a short life time arising from problems caused by zinc mass redistribution, undesirable changes in zinc morphology and the influence of zinc ions on the opposite electrodes. Because nickel-zinc and manganese dioxide-zinc systems are otherwise suitable for electric vehicle propulsion, an effort to develop a long-lasting storage battery is very desirable. One avenue is to find a better electrode separator for such systems.

A separator in an accumulator with a zinc electrode has dual specific role – to provide a mechanical barrier to the growth of zinc dendrites and to protect the cathode active material from diffusing $\text{Zn}(\text{OH})_4^{2-}$ ions that can influence its ability to be charged.

Many different types of separators were under investigation in the past (1). The best results were achieved with microporous separators (2–4) and ion-exchange membrane separators (5–7). Microporous separators show slower redistribution of Zn material compared to ion-exchange membranes, but they have less favorable zinc exclusion selectivity. In this work, an attempt is made to merge the good attributes and to avoid some of the disadvantages of the two types of separators and to prepare a composite separator with slow redistribution of zinc material, better ion exclusion and good conductivity. Polypropylene membranes were chosen as suitable microporous separators which were then coated with Nafion to afford increased ionic selectivity.

Experimental

A special cell suitable both for membrane impedance measurements and for determination of the amount of transported Zn ions, without intervening with the membrane, was designed. The cell, based on the EG&G polarographic cell, allows simple manipulation of different membranes, application of electric field during ion transport and using of inert atmosphere. The part of the cell with the membrane mounted on its bottom

(1, Fig. 1 and 2) is common for both the ion transport and membrane resistance measurements. Its volume is 40 ml. Different cell containers are used for the two types of measurements, as shown in Fig. 1 and 2.

Celgard 3401 and Celgard 3501 (Hoechst Celanese Corp., Charlotte, NC) microporous separators were chosen because they are proven to have slow redistribution of zinc material, good mechanical properties and good chemical resistivity. The name Celgard is a registered trade name of Hoechst Celanese. Typical reported porosities for Celgard 3401 and Celgard 3501 are 38 % and 45 % respectively, the pore dimensions are (width x length) $0.05 \times 0.125 \mu\text{m}$ and $0.075 \times 0.25 \mu\text{m}$ and thickness for both $25 \pm 2.5 \mu\text{m}$. The electrical resistance of the hydrophilic versions of the membranes measured by the Celanese procedure is $78 \text{ m}\Omega/\text{cm}^2$ and $39 \text{ m}\Omega/\text{cm}^2$, respectively.

These membranes are normally supplied in a hydrophilic form which is achieved by treatment with a cationic/nonionic surfactant. For the purpose of some of the experiments a hydrophobic membrane was prepared. The surfactant was removed by multiple washing in methanol of analytical grade.

The membranes were cut into needed size before the modifying treatment. After the treatment, they were attached to the cell either by wrapping with a teflon tape or by tightening under a special hollow nut. Exposed area of the membrane was 2.2 cm^2 .

As a membrane modifying material a solution of cation exchange polymer prepared from Nafion 117 membrane (E. I. DuPont de Nemours & Co., USA, Nafion is a registered trademark) was used. It was either a 5 % Nafion solution in a mixture of lower aliphatic alcohols and 10 % water, commercially available from Aldrich, or an aqueous solution prepared according to Weber, Kavan and Štícha (8) from the Aldrich soluble Nafion.

The Celgard membranes were coated with Nafion from its alcoholic or aqueous solutions at room temperature. Table I lists properties of membranes prepared by several procedures. Sample No. 5 was immersed in a mixture of 1 ml Nafion (5 % Nafion in alcoholic solution) diluted with 3 ml of propanol. Sample No. 4 was soaked in the same

mixture, further diluted by additional 3 ml of propanol. Sample No. 3 was soaked in a Nafion solution with 6 more milliliters of propanol added. Previously weighted dry hydrophobic membranes were immersed for 1 hour in the described mixtures and then dried in the air at room temperature to a constant weight. Another way was to impregnate the membrane at elevated temperature. It was boiled in a solution of Nafion and methanol (0.1 % of Nafion in the mixture) under a reflux condenser for approximately one hour, and allowed to cool either in the solution or in the air. This procedure did not generate coverages significantly different from those obtained by immersion in cold solutions. Yet another method used to impregnate the membranes was to immerse them in a mixture of Nafion and methanol under partial vacuum, in an ultrasonic bath or both. The expected purpose of this effort was to expel any gas trapped inside the membrane. A variation of this method was to apply vacuum suction on the membrane and express the Nafion solution of desired concentration through the membrane. In some cases an aqueous rather than alcoholic Nafion solution has been used. Alcohol dissolves the original hydrophilic coating of the membranes, therefore the membranes impregnated with Nafion dissolved in alcohol are likely to lose their surfactant. On the other hand, if surfactant was needed for membrane modification, it was obtained as an alcoholic extract from washing a stock supply of new hydrophilic membranes. 100 cm² of new membranes were boiled in 50 ml of methanol for 30 minutes under a reflux condenser.

Fisher Certified A.C.S. chemicals and twice distilled water were used. KOH contained reported 0.0005 % of iron and 0.0003 % of heavy metals (as Ag). ZnO contained 0.001 % of lead and 0.0005 % of iron. A 6 mol/l KOH solution was used in all experiments. $\text{Zn}(\text{OH})_4^{2-}$ ion transport was studied on a solution prepared as 0.1 mol/l ZnO dissolved in 6 mol/l KOH.

Polarography was used to measure $\text{Zn}(\text{OH})_4^{2-}$ transport across the membranes. Zinc concentration was determined using a mercury dropping electrode and a Princeton Applied Research Polarographic Analyzer Model 364. The cell arrangement from Fig. 1 was used

with a Hg/HgO reference electrode filled with 6 mol/l KOH and equipped with a Luggin capillary. A linear calibration curve was obtained from wave heights of standard Zn(OH)_4^{2-} solutions in concentration range 0.2 – 10 mmol/l. Zinc limiting current was read at – 1.5 V *vs.* Hg/HgO, with a background current measured at – 1.2 V subtracted.

Frequency dependent electrical impedance was studied using either a Solartron 1255 Frequency Response Analyser in conjunction with the 1286 Solartron Electrochemical Interface or a Hewlett-Packard Impedance Analyzer Model 4192A. The AC perturbation signal was in all cases 10 mV.

Results and discussion

The differences between commercial uncoated membranes in their hydrophilic form, hydrophobic form without the surfactant and the membranes coated with Nafion were studied by measuring the modulus of impedance ($|Z|$) and the phase shift (φ) for the membranes. Data for five different membranes are in Table I.

The membrane No. 2 is without a surfactant and any other coating and it is effectively hydrophobic. Therefore it exhibits a higher $|Z|$ throughout the experimental range (100 Hz – 1 MHz). The phase shift φ is close to zero, which suggests that the membrane behaves as a resistor in an equivalent circuit.

The surfactant coating on the commercially supplied membrane (sample No. 1) increases the conductivity significantly, presumably due to wettability of the membrane and exclusion of trapped air.

The frequency dependence of $|Z|$ and φ between 100 Hz – 1 MHz is not as invariant as it is for membrane No. 2. The lower measured resistance ($|Z| = 46 \text{ m}\Omega/\text{cm}^2$) results simultaneously in higher capacitive component of the membrane.

Membrane Celgard 3501 coated with 0.024 mg/cm^2 of Nafion and without any surfactant (sample No. 3) had $|Z|$ slightly below $10 \Omega/\text{cm}^2$ and it was nearly constant throughout the experimental frequency range. The phase shift φ was close to zero. With increasing mass of Nafion deposited on the membrane (0.047 mg/cm^2 for No. 4), the value of $|Z|$ became smaller, in the range of 1.7 to $1.9 \Omega/\text{cm}^2$, with larger frequency dependence. Similarly, φ varied appreciably more than for sample No. 3, between zero and ten degrees.

Membrane No. 5 had the largest deposited mass of Nafion and its impedance characteristics exhibited the largest frequency dependence of $|Z|$ and φ . As the mass of the deposited Nafion increased, the impedance modulus decreased and hence the membrane conductivity increased. Concurrently, a higher phase shift at higher frequencies and generally a greater dependence on frequency was observed for membranes with higher Nafion loading.

Transport of the Zn(OH)_4^{2-} ions through a Nafion coated membrane was studied by monitoring changes in zinc ion concentration inside the vessel 1 of Fig. 1. Since the inside solution was stirred, the polarographic response gave reliable information about the rate of zinc transport through the film. Zinc transport, driven by concentration gradient, was increasing with the increasing amount of Nafion deposited in the membrane. The impedance values and the flux of zinc transport for several Nafion treated membranes are summarized in Table I.

It is possible to estimate an apparent diffusion coefficient of zinc ions in the membrane from the fluxes listed in the last column of Table I. It holds that

$$D = -\frac{j}{\text{grad } c} = -\frac{j \Delta x}{\Delta c} \quad (1)$$

The membrane thickness Δx was $25 \times 10^{-4} \text{ cm}$ and the zinc ion concentration gradient between two baths at 0.0 mol/l and 0.1 mol/l was $\Delta c = -1.0 \times 10^{-4} \text{ mol/cm}^3$. Thus the apparent diffusion coefficient for zinc in the membrane with 0.047 mg/cm^2 of Nafion was $1.14 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. This is consistent with values expected for such membranes.

The commercial hydrophilic form of Celgard 3401 with surfactant has reported value of electrical resistance (maximum value) $39 \text{ m}\Omega/\text{cm}^2$. The effect of the surfactant on the membrane impedance in the presence of Nafion coating is seen in Table II. Both membranes were made first hydrophobic by rinsing their surfactant off by alcohol. Then one of them was coated from alcoholic solution containing 1 % Nafion, whereas the second was coated in the same solution containing in addition surfactant. The coating was done in an ultrasonic bath.

For a membrane without a surfactant, coated in a 1 % solution of Nafion, no zinc ion transport was detected during a five-hour experiment. The impedance modulus at 50 kHz was quite high, 186Ω . This resistance was probably caused by excess of Nafion on the membrane surface blocking the pores, which was typical for this type of treatment. Use of surfactant decreased the impedance modulus significantly to $330 \text{ m}\Omega$. Similarly, an increase in zinc ion flux through the membrane was observed as shown in Table II. The surfactant increased the membrane conductivity, but at the expense of enhanced zinc ion transport, a property undesirable for a practical storage battery application.

Figure 3 shows the correlation between impedance modulus recorded at 50 kHz and the membrane ability to pass zinc ions. Results for uncoated membranes as well as membranes coated in the various ways described above, are presented in the figure. It is obvious that presence of Nafion hinders zinc ion transport. It also increases the resistivity of the membrane, but this dependence is not linear. In Fig. 3 there are four groups of data points. The group of squares (\square) represents values for commercial membranes in their hydrophilic form without any Nafion coating. To understand the effect that electric field applied across the membrane has on ion transport, a series of experiments was performed in which ion flux through the membrane was measured at a condition in which a steady current was applied across the membrane. Positive field increased zinc ion transport as expected, because in the basic solution zinc exists in the solution as an anion. The flux increase at applied current density of $5 \text{ mA}/\text{cm}^2$ was about 10 % higher than flux maintained only by concentration gradient for either type (3401 and 3501) of the membrane. The

flux/impedance results that correspond to that particular membrane with the flux enhanced by current flow are shown in Fig. 3 by crosses (*). Similarly, a negative field decreased the flux of zinc.

Remaining points were measured without applied electric field. The region of the triangles (Δ) consists of responses by a group of membranes with a surfactant, coated by Nafion, using the several procedures described in the experimental part. The group of circles (o) represents the membranes coated with an excess of Nafion and mainly stripped of the surfactant. It is evident that in these cases the membranes are nearly impermeable for the zincate ions but their resistance is also so high that they are of no practical value for applications in the types of power sources mentioned in the introduction.

The section of triangles (Δ) is very promising for the power sources application although it has a higher resistance than membranes without any treatment. These types of membranes with good conductivity are used in practice although zinc flux is relatively high and it is further enhanced by charge flow during operation of the source. The filled symbols (A, B, C, D, E) in Fig. 3 are experimental values with conditions further specified in the legend for the figure and listed in Table I.

Table III lists results obtained with Celgard 3501 membrane which was impregnated by vacuum-suction of 5 ml (2 ml in the case of the 1 % solution) of an alcoholic Nafion solution of desired concentration through the membrane fastened to the polarographic cell. Although the membrane was originally in its hydrophilic version, suction of excess methanol (10 ml) through it rinsed the surfactant off the membrane. For comparison, the last membrane in Table III was additionally treated with surfactant.

Comparison of the first value from this table and the result obtained with a membrane that was coated using the same Nafion solution in an ultrasonic bath (Tab. II) reveals that the suction method produces more conductive membranes but with correspondingly higher value of zinc flux. On the other hand, with lowering Nafion concentration, this technique produces membranes with increasing resistivity. In all these

cases the measured zinc flux was zero which is expected due to the high overall resistivity. The surfactant significantly decreased the resistivity and increased the zinc ion flux. The flux through the Nafion+surfactant membrane is about two thirds that of the original uncoated hydrophilic membrane.

A number of membranes was prepared using techniques described in the experimental part. In most cases the behavior of the treated membranes varied very little with the method of preparation. Their impedance shortly after immersion in 6 mol/l KOH was relatively very high (typically 1 – 15 k Ω) while the phase angle was in tens of degrees and up to 90°. It is apparent that the membrane behaves shortly after immersion mainly as a capacitor. After several minutes the impedance fell to 10 – 100 Ω and the phase angle was typically below one degree. In such a case the membrane can be described as a resistor in an equivalent circuit. These values level off and became almost constant within the measured period up to 24 hours. Typical results are shown in Fig. 4. Similar results, for which a graph is not given, were obtained using aqueous Nafion solution.

The suction method was the most successful in terms of obtaining a membrane with relatively high conductivity. By contrast, membranes treated by simple dipping in Nafion had higher resistance and long time was required after immersion into a solution for the electrical parameters to stabilize. Figure 4 shows time changes of impedance for a Celgard 3501 in a hydrophobic form as a response to immersion in 6 mol/l KOH. These membranes were coated by immersion in Nafion of several different concentrations. In comparison with Table III, that lists properties of membranes impregnated by suction, it is obvious that simple immersion in Nafion solution of the same concentration leaves the membrane with much higher resistance. Curve A and the first value in Table III correspond to the same Nafion stock solution concentration but the resistance of the dip-coated membrane is more than hundred times higher. It is likely that at this concentration Nafion covers the surface of the membrane, without significant penetration, and traps inside insulating air. Curve B for lower Nafion concentration and corresponding higher conductivity is probably the result of

lower surface concentration and deeper penetration of Nafion inside the membrane. Curves *C* and *D* which are responses of progressively lower concentrations of Nafion exhibit high resistances, comparable to those obtained with the suction method. In both cases, the amount of Nafion available for membrane modification is too low and the membranes remain largely uncoated.

It is obvious that the method of a solution suction through the membrane is the preferred way if Nafion coverage throughout the membrane is desired. The time dependence observed in Fig. 4 also shows that a lower and steady state resistance of the membranes is reached after about 2 hour immersion in the bathing electrolyte. From that time on the resistance values remain virtually constant over a period of several days, which indicates that the applied Nafion modifier is durable.

Conclusions

It has been shown in this work that combination of the ionomer amount and the method how it is applied to the membrane is one possible way how to modify the desired attributes of microporous membranes. Nafion as an ion exchange polymer has been used in this work as a possible modifier influencing selectivity and flow of $\text{Zn}(\text{OH})_4^{2-}$ ions. The study of Nafion trapped in membrane pores is particularly important for better understanding of microheterogeneous systems where the intricate channels of Nafion are of interest. A significant role of a surfactant in its combination with an ionomer has been shown. Inverse dependence of membrane conductivity and the flux of the $\text{Zn}(\text{OH})_4^{2-}$ ions through the microporous membrane, experimentally obtained from work with variously modified membranes, reveals that a very fine balance of several factors (type and amount of the ionomer, its spatial distribution in the microporous membrane, kind, presence and quantity of the surfactant and the presence of the electric field) account for the ion selective

membranes with high conductivity. The method of application of Nafion to the membrane by the suction technique is to be preferred if membranes with high conductivities are desired. By adjusting the parameters and procedures of coating, a membrane with optimized resistance and ion exclusion properties can be prepared.

Acknowledgements

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Legend for figures:

- Fig. 1. Membrane holder in the arrangement for polarographic measurement of transport of $\text{Zn}(\text{OH})_4^{2-}$ ions across the membrane. 1 – polarographic vessel, 2 – bottom container (on a magnetic stirrer, with a stir-bar inside), 3 – membrane, 4 – mercury collector, 5 – 6 mol/l KOH with 0.1 mol/l ZnO, 6 – 6 mol/l KOH, 7 – mechanical stirrer, *CE* – counter electrode, *RE* – reference electrode, *MDE* – mercury dropping electrode, (*Aux*) – auxiliary electrode separated by a frit, used in current flow measurements, N_2 – nitrogen gas inlets.
- Fig. 2. Membrane holder in the arrangement for impedance measurements. 1 – polarographic vessel identical to the one in Fig. 1., 2 – lid with electrodes, 3 – bottom container with electrodes, 4, 5 – potential electrodes, 6, 7 – current electrodes, 8 – membrane.
- Fig. 3. Relationship between the absolute impedance modulus measured at 50 kHz and zinc flux across several types of membranes. Areas (○) and (Δ) are Nafion coated membranes (○ – without surfactant, Δ – with surfactant). More conductive uncoated membranes are in region (□) and in region (×) which is the same membrane with transport enhanced by applied electric field. The filled symbols are the values listed in the Tab. I. A – uncoated membrane with surfactant, B – 0.079 mg/cm² Nafion, C – 0.047 mg/cm² Nafion, D – 0.024 mg/cm² Nafion, E – uncoated membrane without surfactant.
- Fig. 4. Time dependence of the impedance modulus measured at 50 kHz for a membrane Celgard 3501 (hydrophobic form) dip-coated in alcoholic solutions of Nafion of different concentrations. A(×): c = 0.8 %, B(•): c = 0.1 %, C(Δ): c = 0.05 %, D(□): c = 0.025 %.

Tables:

Table I. Dependence of the impedance modulus of the membrane and the flow of zinc through it as a function of modifications of the membrane.

Membrane Celgard 3501			
Sample No.	Nafion [mg/cm ²]	Z [Ω/cm ²] at 50 kHz	j [10 ⁻⁶ mol cm ⁻² hr ⁻¹]
1	0 + surfactant	0.046	34.0
2	0 - no surfactant	138.0	0.0*
3	0.024	9.850	0.36
4	0.047	1.684	1.6
5	0.079	0.250	12.0

* None detected for first 5 hours

Table II. Zinc ion flux and absolute impedance of the Nafion coated membrane with and without surfactant. Coated with 1 % Nafion in ultrasonic bath.

Membrane Celgard 3401		
Surfactant [yes/no]	j [10 ⁻⁶ mol cm ⁻² hr ⁻¹]	Z [Ω cm ⁻²]
no	0*	186.0
yes	16.4	0.330

* None detected for first 5 hours

Table III. Membranes prepared by the vacuum-suction method.

Membrane Celgard 3501		
% of Nafion in the solution	j [10^{-6} mol cm^{-2} hr^{-1}]	$ Z $ [Ω cm^{-2}]
1.0	14.6	0.685
0.1	0	4.37
0.025	0	41.5
0.005	0	73.0
0.005 + surfactant	20.0	0.26

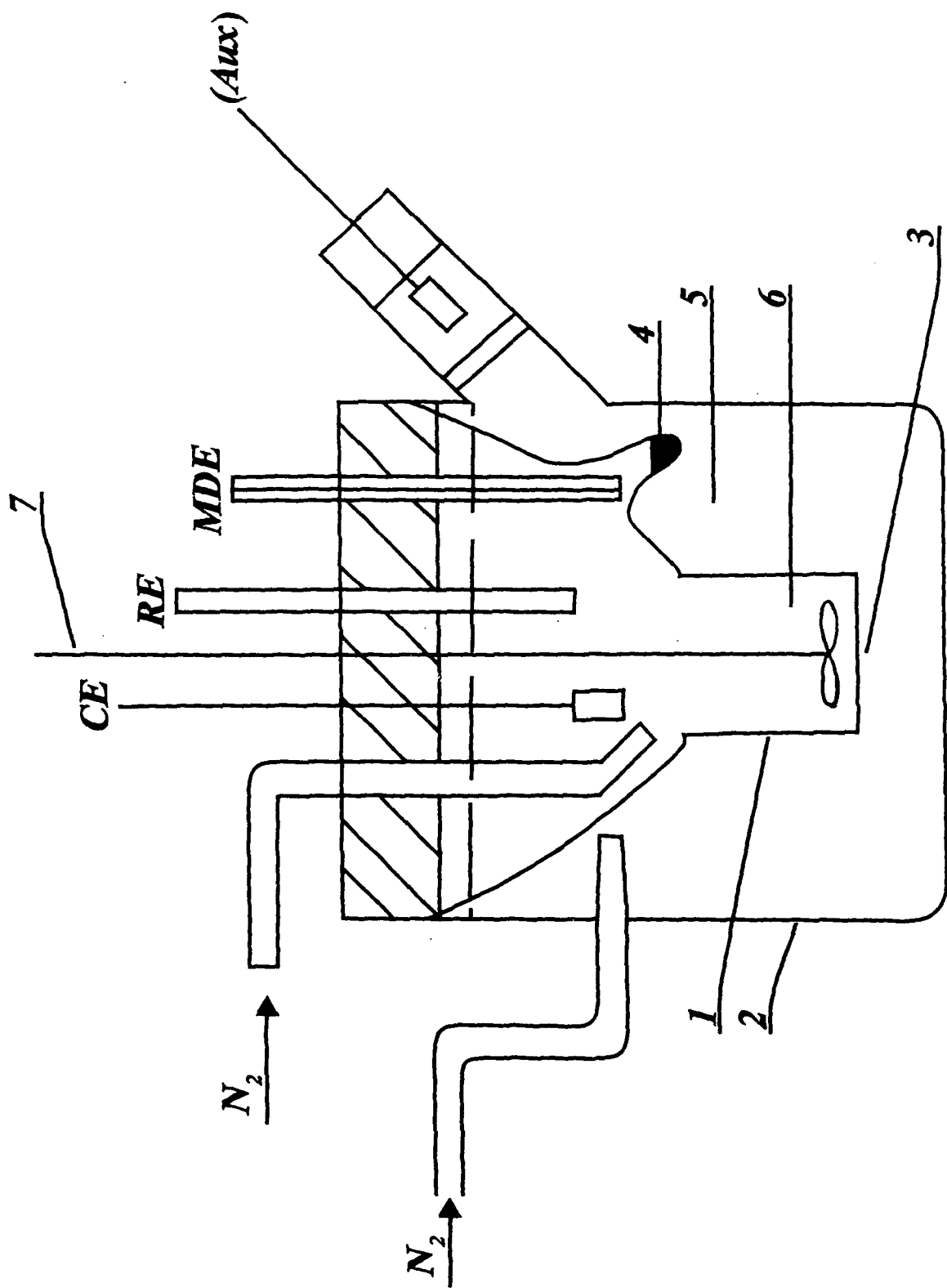


Fig. 1

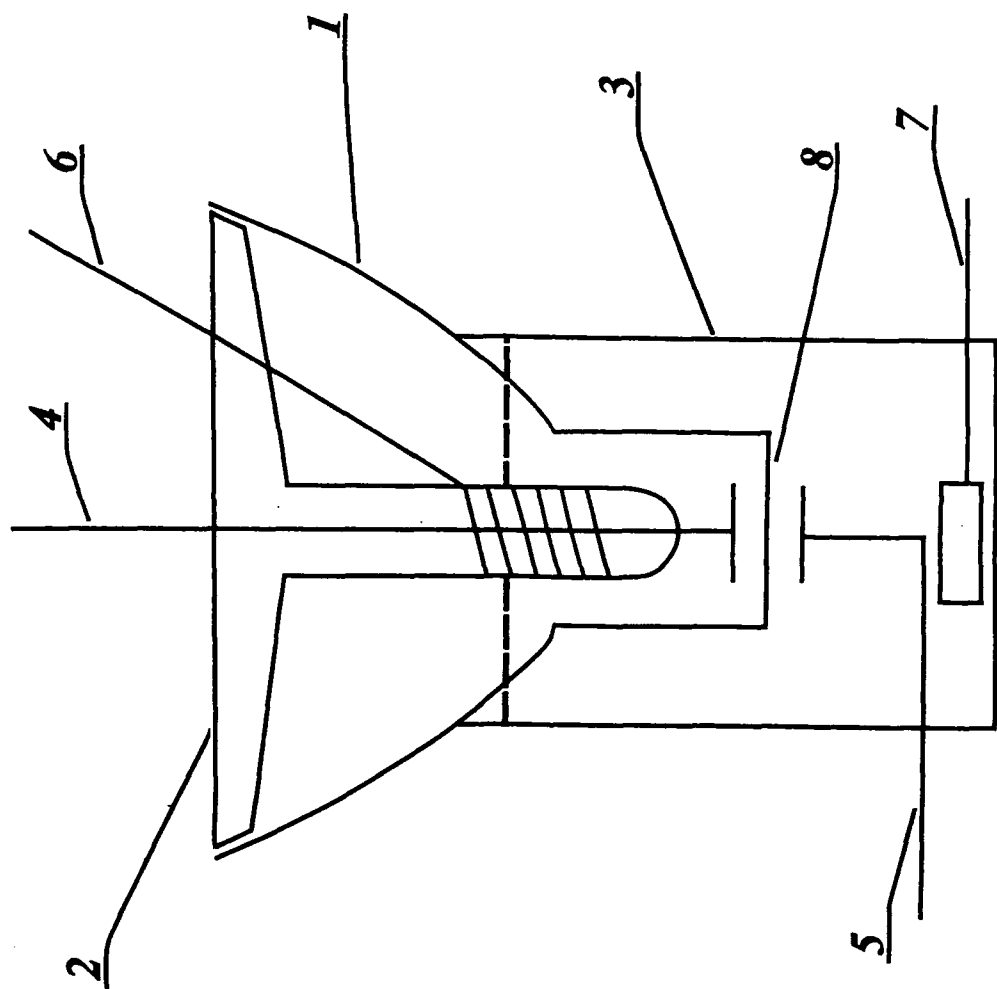


Fig. 2

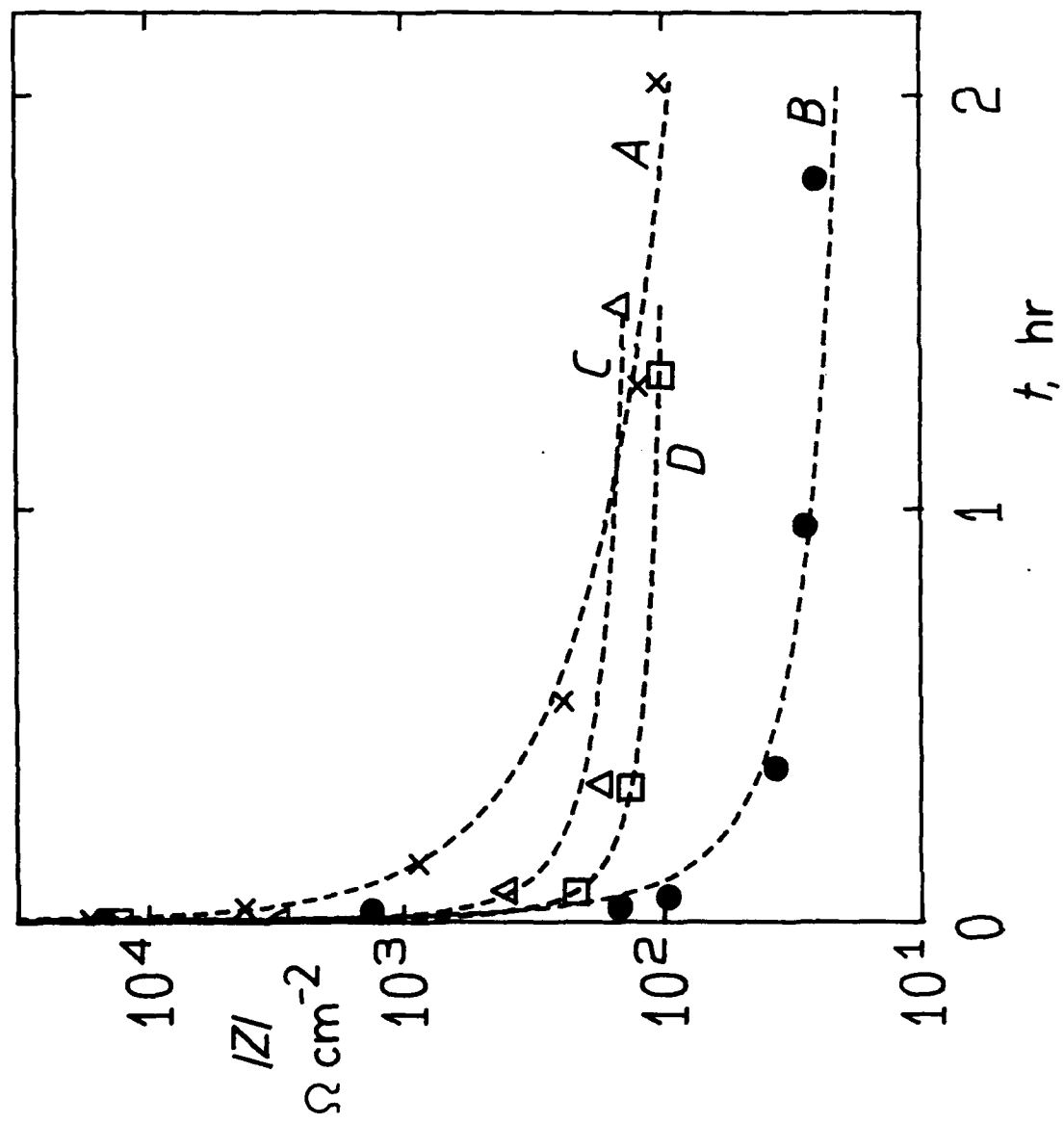


Fig. 3

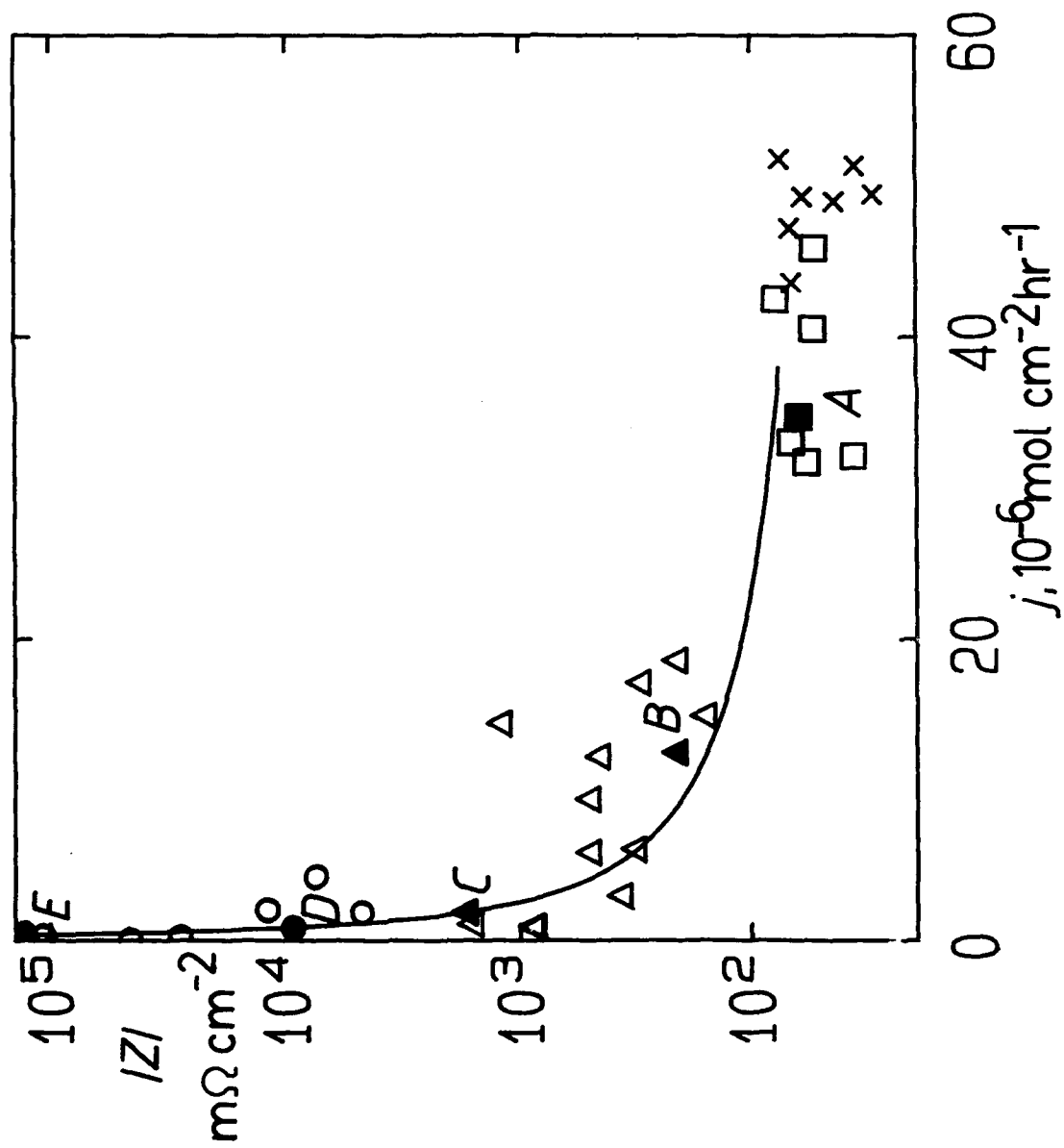


Fig. 4

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